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- (71) Applicant: **ISP INVESTMENTS INC.** [US/US]; 300 Delaware Avenue, Wilmington, DE 19801 (US).
- (72) Inventors: **BEESTMAN, George, B.**; 9 Southwick Circle, Madison, WI 53717 (US). **NARAYANAN, Kolazi, S.**; 33 Carol Place, Wayne, NJ 07470 (US).
- (74) Agents: **MAUE, Marilyn, J.** et al.; International Specialty Products, Legal Dept., Building 10, 1361 Alps Road, Wayne, NJ 07470 (US).
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(54) Title: EMULSIFIABLE CONCENTRATE OF A WATER-INSOLUBLE FUNGICIDE

(57) Abstract: A clear emulsifiable concentrate of a water-insoluble fungicide, without nonylphenol ethoxylate, that can be diluted in water to produce an aqueous ready-to-use formulation free from crystal formation or decomposition.

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EMULSIFIABLE CONCENTRATE OF A  
WATER-INSOLUBLE FUNGICIDE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a delivery system for agriculturally active chemicals, and, more particularly, to an efficacious emulsifiable concentrate for delivering a water-insoluble fungicide at a high loading that can be diluted in water to create a ready-to-use formulation free from crystal formation or decomposition.

2. Description of the Prior Art

Agriculturally active chemicals are most preferably applied in the form of aqueous emulsions, solutions or suspensions. Occasionally, they may also be applied in the form of a dust wherein the active ingredient is adsorbed onto or mixed with a finely divided inert carrier material, such as, china clay, or the like. With such powdered or dust compositions, drift due to wind is a problem and consequently, liquid formulations are preferred.

One of the problems with such liquid formulations is the fact that chemicals having agricultural activity often exhibit extreme insolubility in water. This results in their having to be dissolved either in organic solvents or utilized in the form of emulsions or suspensions. With respect to the use of organic solvents, emulsions concentrates, when highly diluted into water, will not retain the active chemical, resulting in crystal growth that will inhibit biological efficacy and plug spray nozzles. Similarly, with suspension concentrates, once diluted into water, crystal growth becomes a serious problem.

These disadvantages are especially critical when it is desired to produce a ready-to-use formulation that is highly diluted into water.

Strobilurins are a new and highly effective class of fungicides; however, their water solubility is often less than one ppm. Furthermore, they are susceptible to decomposition and crystal growth in aqueous formulations. One such strobilurin, CGA 279202, has a water solubility of only 0.6 ppm, and is susceptible both to crystal growth and to decomposition.

Related references in this field are: U.S. Patent Nos. 5,597,574; 5,672,353; 5,731,264; 5,766,615; 5,834,400; 5,928,992; 6,024,972 and 6,033,681.

Accordingly, it is an object of this invention to provide an emulsion concentrate that is dilutable with water to provide ready-to-use aqueous emulsion formulations of water-insoluble fungicides such as strobilurin that are free from crystal formation and decomposition.

#### SUMMARY OF THE INVENTION

What is provided herein is a clear emulsifiable concentrate of a water-insoluble fungicide, e.g. strobilurin, without using nonylphenol ethoxylate, that can be diluted in water to produce an aqueous ready-to-use formulation free from crystal formation or decomposition. The composition consists essentially of, by weight:

- (a) 0.5 – 25% of water-insoluble fungicide, e.g. strobilurin;
- (b) 5 – 60% of a water-insoluble organic solvent, e.g. aromatic petroleum distillate;
- (c) 5 – 60% of a water-insoluble, polar organic co-solvent, e.g. N-octyl pyrrolidone or propylene carbonate;
- (d) 5 – 60% of an anionic emulsifier, e.g. calcium dodecyl benzene sulfonate;

- (e) 0 - 30% of a free acid anionic emulsifier, e.g. dodecyl benzene sulfonic acid;
- (f) 5 - 30% of a water-insoluble polymer with hydrophobic and hydrophilic groups, e.g. C<sub>16</sub>-C<sub>20</sub> alkyl pyrrolidone polymer, or co-polymer of vinylpyrrolidone/vinylacetate

A matrix composition of the emulsifiable concentrate, i.e. without fungicide, also is provided herein, as well as aqueous ready-to-use formulations, i.e. concentrate plus water.

### DETAILED DESCRIPTION OF THE INVENTION

#### Component Trade Names

Agrimer AL-22 A pyrrolidone polymer containing 80% C<sub>16</sub> alkylation

Agrimer AL-25 A pyrrolidone polymer containing 50% C<sub>16</sub> alkylation

Agrimer AL-30 A pyrrolidone polymer containing 80% C<sub>20</sub> alkylation

Agrimer VA-3 A Co-polymer containing 30% vinyl pyrrolidone and 70% vinyl acetate

Agrimer VA-5 A Co-polymer containing 50% vinyl pyrrolidone and 50% vinyl acetate

AgsolEx BLO gamma-Butyrolactone solvent

AgsolEX 1 N-methyl-2-pyrrolidone solvent

AgsolEx 8 N-n-octyl-2-pyrrolidone

Ca/H DDBSA 50% Dodecyl benzene sulfonic acid, Calcium:free acid 5:1 mixture in Aromatic 150 petroleum solvent

CGA279202 Methoxyimino-{2-[3-(trifluoromethyl-phenyl)-ethylideneamino-oxymethyl]-phenyl}-acetic acid methyl ester

Azoxystrobin Methyl(E)-2-2-6-(2-cyanophenoxy)pyrimidin-4-yloxyphenyl-3-methoxyacrylate

Kresoxin-methyl Methyl(E)-methoxyimino-[alpha-(o-toluloxo)-o-tolyl]acetate

Strobilurins are a class of well known and widely-used water-insoluble fungicides of which CGA 279202, Azoxystrobin, and Kresoxin-methyl are representative examples. In accordance with the invention, a clear, emulsifiable concentrate of such fungicides, free of nonylphenol ethoxylate, that was diluted in water to produce an aqueous ready-to-use formulation free from crystal growth or decomposition, was made with the following components, in parts by weight.

TABLE 1  
EMULSIFIABLE CONCENTRATE OF THE INVENTION

	Component	Suitable	Preferred
(a)	Strobilurin, a water-insoluble fungicide e.g. CGA 279202	0.5 – 25	1 - 15
(b)	Water-insoluble solvent e.g. Aromatic 150, Aromatic 200, Exxate, Xylenes	5 - 60	10 - 40
(c)	Water-insoluble polar co-solvent e.g. Propylene carbonate, AgsolEX8,	5 – 60	10 - 50
(d)	Anionic emulsifier e.g. Ca-Dodecylbenzene sulfonic acid, alkoxylated tristyryl- phenyl phosphoric acid salts	5 – 60	10 - 50
(e)	Anionic emulsifier free acid/pH buffer e.g. Dodecylbenzene sulfonic acid, alkoxylated tristyrylphenyl phosphoric acid	0 – 30	1 - 25
(f)	Water-insoluble polymer e.g. Agrimer AL-22, Agrimer AL30, Agrimer VA-3 Agrimer VA-5	5 – 30	10 -20

This concentrate was diluted in water to provide a formulation containing 10-500 ppm strobilurin which was a ready-to-use formulation free from crystal development or decomposition.

A matrix composition of the invention also was made which include components (b) through (f), i.e. without the active fungicide, which was added later, to provide the emulsifiable concentrate.

### PREPARATION OF CONCENTRATE OF INVENTION

#### 1. General Procedure

The procedure used to prepare water-dilutable concentrates is described below. These concentrates were screened for use as ready-to-use (RTU) water base formulations containing about 75 ppm fungicide. The emulsion concentrates containing ingredients (a) through (f) were prepared by mixing the ingredients until the polymers were dissolved and a uniform solution was obtained. Then CGA 279202 strobilurin fungicide was added. The resulting uniform, non-separating emulsion concentrate containing strobilurin fungicide was diluted into distilled water to 75 parts fungicide per million parts of water (ppm). Highly diluted concentrates in water were ready-to-use (RTU) finished formulations. Each RTU aqueous dilution was sub-sampled and placed into accelerated aging at 50°C, and 0°C for one month. After accelerated aging, a tiny spec of crystals was added to each RTU as seed crystals to cause crystal formation in any RTU formulation that might be unstable to crystal formation. Each RTU was analyzed by optical microscopy for the presence of crystals and by gas chromatography to test its chemical stability.

## 2. Required ingredients

- (a) Active ingredients: Water insoluble fungicides preferably strobilurins. Examples: CGA 279202, Azoxystrobin and Kresoxin-methyl and others. Concentration in the concentrate: 0.5 – 25%; preferred 1-15%. Use-dilution in water to 10-500 ppm, preferably 50-100 ppm.
- (b) Water-insoluble solvent: Examples: Aromatic petroleum distillate (Exxon 150, or Exxon 200), Hydrogenated alkyl naphthalene, aliphatic hydrocarbons with greater than C<sub>8</sub> fraction, vegetable oil concentration in the concentrate: 5-60%; preferred 10-50%.
- (c) Water insoluble polar co-solvent: Examples: N-alkyl pyrrolidone, preferably NOP (Agsol Ex 8), Propylene carbonate, Esters like Exxate (mixed alkyl acetate with C<sub>5</sub>-C<sub>8</sub> alkyl, with C<sub>6</sub> predominating), alkyl caproate. Concentration in the concentrate: 5-60%; preferred 10-40%.
- (d) (e) Anionic emulsifier: Soluble in both oil and water. Examples: Ca dodecyl benzene sulfonate, preferably partially neutralized with the acid form to render an optimum pH range for stability of the active ingredient in solution. [pH range- 4.0-7.0]. Concentration in the concentrate: 5-60%; preferred 10-50%.
- (f) Water-insoluble polymer: Copolymer with hydrophobic and hydrophilic groups selected from the following: Hydrophobic groups: alkyl graft, vinyl acetate, alkyl vinyl ether (with > C<sub>2</sub> alkyl)acrylic esters, maleic acid esters, and others.

Hydrophilic groups: vinyl pyrrolidone, vinyl imidazolidinone, vinyl imidazole, vinyl caprolactam, maleic acid/salts, acrylic acid/salts and others. Specific examples: Agrimer AL 25, Agrimer VA 5, and Agrimer VA3 (preferably water insoluble copolymers). Concentration in the concentrate: 5-30%; preferred 10-20%.

Optional ingredients:

Polar water soluble solvents, e.g. NMP (Agsol Ex 1), BLO, antifoams e.g. soda soap, silicone oil, rheology modifiers e.g. natural gums, microbial inhibitors e.g. Proxel GXL.

The following examples 1-7 illustrate the invention more fully.



<u>Ingredients</u>	<u>Function</u>	<u>Ex 1</u>	<u>Ex 2</u>
CGA 279202	Active ingredient	0.5	0.5
NOP (Agsol Ex 8)	Polar water insoluble cosolvent	3.8	0
Propylene carbonate	Polar water insoluble cosolvent	0	2.85
Aromatic petroleum distillate 150(Exxon)	Nonpolar solvent	2.85	1.425
Agrimer AL 25	Polymer with hydrophobic and hydrophilic groups	1.425	0
Agrimer VA5		0	1.425
CaH/DDBSA [50% (Ca dodecylbenzene sulfonate+ Dodecylbenzene sulfonic acid (5:1) in Aromatic pet distillate, Exxon 150]	Antonic emulsifier with adjusted pH	1.425	3.8
Total		10	10
<u>Results</u>			
Uniform initial concentration		Yes	Yes
Crystals in 75 ppm dilution after one week, ambient		No	No
Crystals in 75 ppm dilution after one month, ambient		No	No
Crystal after aging and seeding		No	No
CGA 279202 chemical stability		Yes	Yes

<u>Ingredients</u>	<u>Function</u>	<u>Ex 3</u>	<u>Ex 4</u>	<u>Ex 5</u>	<u>Ex 6</u>	<u>Ex 7</u>
CGA 279202	Active ingredient		0.1		0.1	
Azoxystrobin		0.5		0.1		0.1
Kresoxin-methyl						
NOP (Agsol Ex 8)	Polar water insoluble cosolvent				3.96	3.96
Propylene carbonate	Polar water insoluble cosolvent	1.425	1.485	1.485		
Aromatic petroleum distillate 150 (Exxon)	Nonpolar solvent	2.85	2.97	2.97	2.97	2.97
Agrimer AL 22						
Agrimer AL 25	Polymer with hydrophobic and hydrophilic groups				1.485	1.485
Agrimer AL 30		1.425	1.485	1.485		
Agrimer VA5						
Agrimer VA 3		3.8	3.96	3.96	1.485	1.485
CaH/DDBSA	Anionic emulsifier with adjusted pH					
[50% (Ca dodecylbenzene sulfonate+ Dodecylbenzene sulfonic acid (5:1) in Aromatic pet. distillate, Exxon 150]						
Total		10	10	10	10	10
<u>Results</u>		Yes	Yes	Yes	Yes	Yes
Uniform initial concentration		No	No	No	No	No
Crystals in 75 ppm dilution after one week, ambient		No	No	No	No	No
Crystals in 75 ppm dilution after one month, ambient		No	No	No	No	No
Crystal after aging and seeding		No	No	No	No	No

**General Comments:**

**Compositions with Agsol Ex 8 ( NOP) as cosolvent**

A commercially viable emulsion concentrate that is dilutable in water to a 75 ppm RTU formulation, that is free from crystal formation and in which CGA 279202 was chemically stable has been achieved, using Agrimer AL-25 with Agsol Ex 8 as co-solvent. See Example 1.

**Compositions without NOP**

Compositions with water-insoluble Agrimer VA-5 and polar water-insoluble propylene carbonate and anionic emulsifiers were stable to crystal formation after accelerated aging and seeding. See Example 2.

Kresoxin-methyl at 5% (Example 3) forms an emulsion concentrate that can be diluted in distilled water to 75 ppm Kresoxin-methyl and is stable to crystal formation throughout accelerated aging and seeding.

Three different strobilurin fungicides: Azoxystrobin, Kresoxin-methyl, and CGA 279202 are stable to crystal formation in emulsion concentrates that are diluted to 75 ppm RTU formulations when the emulsion concentrates contain a water-insoluble solvent, water-insoluble polar co-solvent, water-insoluble polymer and anionic emulsifier. See Examples 4-7.

**WHAT IS CLAIMED IS:**

1. A clear emulsifiable concentrate of a water-insoluble fungicide, free of nonylphenol ethoxylate, that can be diluted in water to produce an aqueous ready-to-use formulation free from crystal formation or decomposition, consisting essentially of, by weight:

- (a) 0.5 – 25% of said fungicide,
- (b) 5 – 60% of a water-insoluble organic solvent,
- (c) 5 – 60% of a water-insoluble, polar co-solvent,
- (d) 5 – 60% of an anionic emulsifier,
- (e) 0 - 30% of a free acid anionic emulsifier, and
- (f) 5 – 30% of a water-insoluble polymer with hydrophobic and hydrophilic groups.

2. A ready-to-use formulation created by diluting the concentrate of claim 1 to 10-500 ppm fungicide in water which is stable to crystal formation and decomposition.

3. A matrix composition of claim 1 without component (a).

4. A composition of claim 1 wherein (a) is 1-15%, (b) is 10-40%, (c) is 10-50%, (d) is 10-50%, (e) is 1-25% and (f) is 10-20%.

5. A composition according to claim 1 wherein (a) is a strobilurin.

6. A composition according to claim 1 wherein
- (b) is an aromatic petroleum distillate,
  - (c) is N-octyl pyrrolidone or propylene carbonate,
  - (d) is calcium dodecylbenzene sulfonic acid or alkylated tristyryl phenyl phosphoric acid,
  - (e) is dodecylbenzene sulfonic acid, or alkoxylated tristyrylphenyl phosphoric acid, and
  - (f) is a pyrrolidone polymer containing 50-80% C<sub>16</sub> alkylation, a copolymer of 30-50% vinyl pyrrolidone and 50-70% vinyl acetate.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US02/07958

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : A01N 25/00

US CL : 424/405

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/405

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST, STN

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 98/06780 A1 (NARAYANAN et al) 19 February 1998, see abstract, pages 2-3, claim 1.	1-5
Y	US 5,464,627 A (FU et al) 07 November 1995, see claim 1.	1,2,4,5
Y	US 6,033,687 A (NARAYANAN et al) 07 March 2000, see claim 1	1,2,4,5

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"G" document member of the same patent family
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Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

ALTON PRYOR

Telephone No. (703) 308-1234